Final Progress Report: Controlling Hexavalent Americium – A Centerpiece to a Compact Nuclear Fuel Cycle

This report contains the initial scope, objectives and deliverables recovered from the PICS:NE website. Commentary is provided on these aspects, as well as the scientific knowledge and deliverables produced through the project.

Initial Scope

The primary purpose of the research proposed here is to develop sufficient knowledge to exploit the fundamental chemistry of Am to enable an industrially-viable means to co-recover the major and minor actinide elements from used nuclear fuel. This study will be conducted via two separate, but complementary lines of investigation. The first will focus on determining the mechanisms of AmO_2^{2+} reduction in liquid-liquid extraction systems. The second will consider the use of branched extractants to separate hexavalent actinides (U-Am) from the other fuel components.

Commentary: The project succeeded in identifying two of the most problematic aspects in developing a hexavalent americium separation system that most closely parallels the PUREX process: high acid concentration and the diamyl amyl phosphorus reagent. Branched extractant monoamide reagents, which should be selective for hexavalent actinides over tetravalent actinides, were synthesized and tested for oxidized americium recovery but were found as too weak for oxidized americium recovery when paired with the copper periodate oxidant.

Potential Future Work: The sodium bismuthate oxidant may increase the amount of hexavalent americium available in the system at higher acid concentrations and this should be a future consideration for follow on work.

Objectives

1) Identify primary factors leading to hexavalent Am reduction and oxidation. Done (see above)

*2) Evaluate the limitations of various separations systems based on this capability. it*Done (see below)

3) Synthesize and utilize extractants appropriate to hexavalent An recovery. Done (see below)

Commentary: Regarding objective two, a significant limitation was observed regarding the ability to oxidize and recover americium in the presence of a used nuclear fuel (aka ALSEP) simulant. Copper periodate experiments were ran under conditions where the copper periodate was near saturated in the aqueous phase. This did not provide enough oxidative capacity to oxidize the fission products and americium present in the system.

Potential Future Work: Americium oxidation and recovery in the presence of a used nuclear fuel simulant should be considered with sodium bismuthate. Also, even though the copper periodate would initially be partially precipitated, larger excesses of copper periodate should be considered. The reduced divalent copper and iodine would most likely be soluble in the processing scheme and eventually dissolve.

Personnel Supported - Updates

Dr. Jenifer Shafer: Dr. Shafer submitted her tenure package the fall of 2017 and the departmental vote was unanimous. The NEUP awarded to Dr. Shafer was instrumental in supporting her tenure case.

Dr. Kenneth Nash: Dr. Nash will be retiring this spring after at thirty plus (!) year career in actinide science.

Dr. Kevin McCann: Support from the NEUP program were the sole external support of Kevin's graduate career at Colorado School of Mines. Dr. McCann is currently a post-doctoral researcher at Savannah River National Laboratory.

Dr. Joseph Lapka: Dr. Lapka is a post-doctoral associate at Washington State University. His efforts were supported by the NEUP project.

Deliverables

Manuscripts

1. McCann, K.C., Sinkov, S.I., Lumetta, G. J., **Shafer, J.C.*** Inner versus Outer Sphere Metal-Monoamide Complexation: Ramifications for Tetravalent & Hexavalent Actinide Selectivity, *In Review, New J. Chem.*
2. McCann, K.C., Sinkov, S.I., Lumetta, G. J., **Shafer, J.C.*** Spectroscopic Extraction Analysis of Copper(III) Periodate Oxidized Hexavalent Transuranium Actinides, *Revisions in Progress, Ind. Chem. Eng. Res.*
3. Drader, J.; Saint-Louis, G.; Muller, J. M.; Charbonnel, M-C.; Guilbaud, P.; Berthon, L.; Roscioli-Johnson, K.; Zarzana, C.; Groenwald, G.; Mincher, B.J.; Mezyk, S.P.; McCann, K.; Braley, J.C. Radiation chemistry of the branched-chain monoamide di-ethylhexyl-isobutyramide. *Solv. Extr. Ion Exchange, 2017, In Press*.
4. McCann, K.; Drader, J.A.; Braley, J.C.* Comparisons of Actinide Recovery between Branched and Straight-chained Monoamide Extractants. *Sep. Pur. Rev., 2017, In Press.*
5. McCann, K.; Mincher, B.J.; Schmitt, N.C.; Braley, J.C.* Hexavalent Actinide Extraction Using N,N-Dialkyl Amides. Ind. Eng. Chem. Res., 2017, 56 (22), 6515–6519.
6. McCann, K.C.; Brigham, D.; Morisson, S.; Braley, J.C.* Hexavalent Americium Recovery Using Copper (III) Periodate. Inorg. Chem., 2016, 55 (22), 11971–11978.
7. Burn, A.G., Martin, L.R. and Nash, K.L., 2017. Pentavalent Neptunyl ([O≡ Np≡ O]+) Cation–Cation Interactions in Aqueous/Polar Organic Mixed-Solvent Media. Journal of Solution Chemistry, 46(6), pp.1299-1314.

Patent

1. Lapka, J., Huber, M., Nash, K.N., Shafer, J.C. "Acidic organophosphorus separation of americium and curium by utilizing copper periodate oxidant"

Oral Presentations

1. Shafer, J.C., University of Wisconsin. Making Americium Hexavalent Again, Nuclear Engineering Department, September 2017.
2. Shafer, J.C., University of California, Berkeley. Making Americium Hexavalent Again, Nuclear Engineering Department, April 2017.

3. Lapka, J., Nash, K.L. Oxidation and Separation of Americium by Peroxydisulfate, 19th Separation Science & Technology Conference, Gatlinburg, TN, October 2016.
4. Shafer, J.C., San Jose State University. Separations in Actinide Science, June 2016.
5. McCann, K.; Braley, J.C. Achieving hexavalent actinide separations using copper(III) periodate, 40th Actinide Separations Conference, San Diego, CA, May 2016
6. McCann, K.; Braley, J.C. Reduction of Copper and Silver in Unconventional Oxidation States, 40th Actinide Separations Conference, Salt Lake City, UT, May 2015
7. Shafer, J.C., Applied Actinide Chemistry 101: Separations relevant to used nuclear fuel, Physics Department Colloquium, Colorado School of Mines, February 2015

Research Highlights

- The recovery of oxidized americium (D>1) from molar acid media was demonstrated using both DAAP and straight chain monoamide extractants.
    - DAAP is strongly reducing towards hexavalent americium
    - Monoamide reagents are not
        - The reason for this is still not clear
- Copper and silver periodates and pertellurates were assessed for am oxidation. Copper periodate was found to be the most efficient.
- The recovery of macroscopic amounts of americium by DAAP using the copper periodate oxidant was demonstrated
    - Spectroscopic studies of the organic phase show DAAP recovered americium following copper periodate oxidation is present as a mixture of oxidation states that vary over time
    - Other actinides (U-Pu) are stable in the hexavalent state after extraction to the organic phase
- The slow step in americium oxidation by copper periodate seems to be the acid catalyzed dissociation of the periodate ligand from the copper center. This suggests an inner sphere electron transfer is responsible for americium oxidation/copper reduction.
- Single state separation factors on the order of 100-1000 between Am and Cm are possible using the copper periodate oxidant and a cation exchange reagent. A flat pH dependence is observed for this separation and a patent is pending.
- A significant limitation to this technology will be providing enough oxidation capacity to oxidize americium and all the other fission products present during used nuclear fuel reprocessing.

Proposed Future Work

- Americium oxidation and recovery in the presence of a used nuclear fuel simulant should be considered with sodium bismuthate.
- Recovery of hexavalent Am by branched monoamides in the presence of sodium bismuthate.
- Assessment of the sodium bismuthate oxidation mechanism
- Development of sodium bismuthate nanomaterials for controlled dissolution of the reduced bismuth(III)
- Assess other ligands to stabilize or increase the solubility of higher oxidation state metals.